

**(12) UK Patent Application (19) GB (11) 2 294 269 (13) A**

**(43) Date of A Publication 24.04.1998**

**(21) Application No 9421220.6**

**(22) Date of Filing 21.10.1994**

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**(51) INT CL<sup>6</sup>**

**C11D 3/08 3/386 // ( C11D 1/14 1:72 )**

**(52) UK CL (Edition O)**

**C5D DHC D107 D111 D112 D118 D120 D121 D125 D127  
D142 D149 D166 D173 D179 D180 D182**

**(56) Documents Cited**

**EP 0552054 A1 EP 0521635 A1**

**(58) Field of Search**

**UK CL (Edition N) C5D DHC DHZ DJA DJX  
INT CL<sup>6</sup> C11D**

**(54) Detergent composition**

**(57) A detergent composition which comprises a surfactant selected from anionic, nonionic, cationic, amphoteric and zwitterionic detergent-active compounds and mixtures thereof; a detersity builder comprising zeolite P having a silicon to aluminium ratio not greater than 1.33 (zeolite MAP); and a cellulolytic enzyme. Preferably the zeolite MAP has a particle size ( $d_{50}$ ) of < 1.0 micrometre.**

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TITLE: DETERGENT COMPOSITION

The present invention relates to a detergent composition and, in particular, to improvements in the detergency performance of laundry detergent compositions comprising zeolites as a sequestering agent for water hardness.

Detergent compositions for heavy-duty fabric washing conventionally contain detergency builders which lower the concentration of calcium and magnesium water hardness ions in the wash liquor and thereby provide good detergency effect in both hard and soft water.

Conventionally, inorganic phosphates, such as sodium tripolyphosphate, have been used as builders for laundry detergents. More recently, alkali metal aluminosilicate ion-exchangers, particularly crystalline sodium aluminosilicate zeolite A, have been proposed as replacements for the inorganic phosphates.

For example, EP 21 491A (Procter & Gamble) discloses detergent compositions containing a building system which includes zeolite A, X or P (B) or a mixture thereof. EP 384070A (Unilever) discloses specific zeolite P materials having an especially low silicon to

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aluminium ratio not greater than 1.33 (hereinafter referred to as zeolite MAP) and describes its use as a detergency builder. To date, however, zeolite A is the preferred aluminosilicate detergency builder in commercially available products.

It is also known in the art that detergent formulations containing small particle size zeolites can have advantages over other zeolites in processing of the surfactant, due to the increased surface area of absorption. For example EPA 0521635 (Unilever) discloses a free-flowing particulate detergent composition including zeolite MAP which preferably has a particle size  $d_{50}$  (defined hereinafter) within the range of from 0.4 to 2.0 micrometres and most preferably from 0.4 to 1.0 micrometres.

The quantity " $d_{50}$ " indicates that 50 wt% of the particles have a diameter smaller than that figure. EPA 0522726, EPA 0552053 and EPA 00552054 (Unilever) also all disclose a preference for zeolite MAP having a small average particle size and illustrate detergent compositions in which the zeolite MAP has a particle size ( $d_{50}$ ) of 0.8.

We have found, however, that formulations containing small particle size zeolites ( $d_{50} < 1.0$  micrometres) show a significant increase in fabric encrustation after repeated washing as compared with coarser size zeolites ( $d_{50} > 1.0$  micrometres).

We have surprisingly found that superior detergency effects can be achieved by incorporating in the detergent composition a cellulytic enzyme.

Detergent compositions containing cellulases are known in the art. By using such enzymes in a detergent, it is possible to hydrolyze the celluloses present in stains and soil on the clothes, to such a degree that they become readily soluble in water.

The use of a cellulytic enzyme has benefits in the laundry process, in particular with depilling, clay removal and in achieving a whiter appearance. We have found that the use of zeolite MAP with a cellulytic enzyme leads to significant performance benefits particularly in boilwash encrustation.

According to a particular aspect of this invention we have found that particular advantages accrue in using a cellulytic enzyme in a detergent composition comprising small particle size zeolite MAP such as zeolite MAP having a particle size  $d_{50}$  of  $< 1.0$  micrometre. In particular, the problem of fabric encrustation after repeated washing is reduced or eliminated by means of the present invention.

Thus, the present invention provides a detergent composition comprising:

- a) a surfactant selected from anionic, nonionic, cationic, amphoteric and zwitterionic detergent - active compounds and mixtures thereof;
- b) a detersity builder comprising zeolite P having a silicon to aluminium ratio not greater than 1.33 (zeolite MAP); and
- c) a cellulolytic enzyme.

The cellulolytic enzymes usable in the present invention generally have a molecular weight range of 20kD to 70kD and include both bacterial and fungal cellulolytic enzymes. Preferably, they will have a pH optimum of between 5 and 9.5. Suitable cellulases are disclosed in U.S. Patent 4,435,307, Barbesgaard et al, issued March 6, 1984, which discloses fungal cellulase produced from Humicola insolens and Humicola strain DSM1800 or a cellulase 212-producing fungus belonging to the genus Aeromonas, and cellulase extracted from the hepatopancreas of a marine mollusk (Dolabella Auricula Solander). Suitable cellulases are also disclosed in GB-A-2,075,028; GB-A-2,095,275 and DE-OS-2,247,832.

The enzyme may be incorporated in the granular composition in an amount, for example, of 0.01 to 4% by weight, preferably 0.05 to 2% by weight, most preferably 0.1 to 0.2% by weight at an activity of 1000 cevu/g, to provide respectively 10 to 4000, 50 to 2000 and 100 to 200 cevu per 100 g of composition.

Examples of specific commercially available catalytic enzymes suitable for use in the present invention include Carezyme and Endolase.

Endolase A, for example, may be incorporated in the granular detergent composition in an amount of 0.1 to 3% by weight, preferably 0.5 to 2% by weight at an activity of 1250 cevu/g.

In liquid detergent formulations typical examples of suitable amounts for the cellulolytic enzymes are 0.09% of cellulase at 3000 cevu/g and 0.08% of Endolase A at 5000 cevu/g.

The detergent composition according to the invention contains, as an essential ingredient, one or more surfactants selected from anionic, nonionic, cationic, amphoteric and zwitterionic detergent-active compounds and mixtures thereof. Such surfactants are well known and described in the literature, for example, in "Surface-Active Agents and Detergents", Volumes I and II by Schwartz, Perry and Berch.

Examples of suitable anionic surfactants include alkylbenzene sulphonates, particularly sodium linear alkylbenzene sulphonates having an alkyl chain length of C<sub>8</sub>-C<sub>15</sub>; C<sub>12</sub>-C<sub>15</sub>

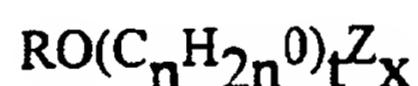
primary alkyl sulphates; olefin sulphonates; alkyl xylene sulphonates; dialkyl sulphosuccinates; and fatty acid ester sulphonates. Sodium salts are generally preferred.

Examples of suitable nonionic surfactants include alkoxylated adducts of fatty alcohols containing an average of from 3 to 10 alkylene oxide groups per molecule. Preferred alkoxylated adducts of fatty alcohols contain an average of less than 5 alkylene oxide groups per molecule, for example less than 4 alkylene oxide groups per molecule e.g. 3.5 and usefully 3 alkylene oxide groups per molecule or less and usefully also greater than 0.5, or 1, or 2 alkylene oxide groups per molecule.

A particularly preferred aliphatic alcohol ethoxylate is a primary alcohol having an average of 12 to 15 carbon atoms in the alkyl chain condensed with an average of three ethoxy groups per mole of alcohol.

Specific examples of suitable alkoxylated adducts of fatty alcohols are Synperonic A3 (ex ICI), which is a C<sub>13</sub>-C<sub>15</sub> alcohol with about three ethylene oxide groups per molecule and Empilan KB3 (ex Marchon), which is lauric alcohol 3EO.

Another class of nonionic surfactants comprises alkyl polyglucoside compounds of general formula



wherein Z is a moiety derived from glucose; R is a saturated hydrophobic alkyl group that contains from 12 to 18 carbon atoms; t is from 0 to 10 and n is 2 or 3; x is from 1.1 to 4, the compounds including less than 10% unreacted fatty alcohol and less than 50% short chain alkyl polyglucosides. Compounds of this type and their use in detergent compositions are disclosed in EP-B 0070074, 0070077, 0075996 and 0094118.

The surfactant will generally be included in the detergent composition in an amount of 5 to 60% by weight, preferably 5 to 40% by weight and most preferably from 10 to 25% by weight of the composition.

According to the present invention the detergency builder system is based on zeolite MAP, optionally in conjunction with one or more supplementary builders. The amount of zeolite MAP employed may range, for example, from 5 to 60 wt%, more preferably from 15 to 40 wt%.

Zeolite MAP is described in EP 384070A (Unilever). It is defined as an alkali metal alumino-silicate of the zeolite P type having a silicon to aluminium ratio not greater than 1.33, preferably within the range from 0.9 to 1.33 and more preferably within the range of from 0.9 to 1.2.

Of particular interest is zeolite MAP having a silicon to aluminium ratio not greater than 1.15 and, more particularly, not greater than 1.07.

Zeolite P having a Si:Al ratio of 1.33 or less may be prepared by the following steps:

(i) mixing together a sodium aluminate having a mole ratio  $\text{Na}_2\text{O}:\text{Al}_2\text{O}_3$  within the range of from 1.4 to 2.0 and a sodium silicate having a mole ratio  $\text{SiO}_2:\text{Na}_2\text{O}$  within the range of from 0.8 to 3.4 with vigorous stirring at a temperature within the range of from 25°C to boiling point usually 95°C, to give a gel having the following composition;

$\text{Al}_2\text{O}_3::(1.75-3.5)\text{SiO}_2:(2.3-7.5)\text{Na}_2\text{O}:\text{P}(80-450)\text{H}_2\text{O};$

(ii) ageing the gel composition for 0.5 to 10 hours, preferably 2 to 5 hours, at a temperature within the range of from 70°C to boiling point, usually to 95°C, with sufficient stirring to maintain any solids present in suspension;

(iii) separating the crystalline sodium aluminosilicate thus formed, washing to a pH within the range of from 10 to 12.5, and drying, preferably at a temperature not exceeding 150°C, to a moisture content of not less than 5 wt%.

Preferred drying methods are spray-drying and flash drying. It appears that oven drying at too high a temperature may adversely affect the calcium binding capacity of the product under certain circumstances.

Commercial sodium metasilicate pentahydrate dissolved in water and commercial sodium silicate solution (waterglass) are both suitable silica sources for the production of zeolite P in accordance with the invention. The reactants may be added together in any order either rapidly or slowly. Rapid addition at ambient temperature, and slow addition at elevated temperature (90-95°C) both give the desired product.

Vigorous stirring of the gel during the addition of the reactants, and at least moderate stirring during the subsequent ageing step, however, appear to be essential for the formation of pure zeolite P. In the absence of stirring, various mixtures of crystalline and amorphous materials may be obtained.

Zeolite MAP generally has a calcium binding capacity of at least 150 mg CaO per g of anhydrous aluminosilicate, as measured by the standard method described in GB 1473201 (Henkel). The calcium binding capacity is normally 160 mg CaO/g and may be as high 170 mg CaO/g.

Although zeolite MAP like other zeolites contains water of hydration, for the purposes of the present invention amounts and percentages of zeolite are expressed in terms of the notional anhydrous material. The amount of water present in hydrated zeolite MAP at ambient temperature and humidity is generally about 20 wt%.

A particularly preferred zeolite MAP for use according to the present invention has a  $d_{50}$  of < 1.0 micrometre, for example 0.4 to 1.0 micrometres.

The particle size is determined by conventional analytical techniques such as, for example, microscopic determination utilizing a scanning electron microscope or by means of a laser granulometer.

Zeolite MAP having the required small particle size according to one aspect of the present invention can be prepared by the conventional techniques as described above while adopting one or more of the following steps:-

- a) increasing crystallisation temperature and reducing crystallisation time;
- b) increasing the size of the seed crystals used to produce the zeolite;
- c) feeding the aluminosilicate gels into the crystallisation stage immediately after they form (i.e. eliminate ageing of gels);
- d) screening the zeolite product to remove fine material.

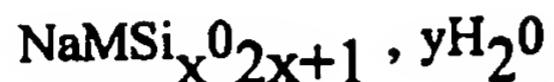
According to one embodiment of the invention the zeolite MAP detergent builder is in powder form.

For convenience in handling, however, the material may be granulated by conventional techniques such as spray drying or by a non-tower method to form larger particles.

In the granular detergent compositions according to the invention, the detergency builder can be zeolite MAP alone or a combination of zeolite MAP with an organic or inorganic cobuilder.

Suitable organic cobuilders can be monomeric or polymeric carboxylates such as citrates or polymers of acrylic, methacrylic and/or maleic acids in neutralised form. Suitable inorganic cobuilders include carbonates, and amorphous and crystalline lamellar sodium silicates.

Suitable crystalline lamellar silicates have the composition:



where M is sodium or hydrogen, preferably sodium; x is a number from 1.9 to 4; and y is a number from 0 to 20. Such materials are described in US Patents No. 4664839; No. 4728443 and No. 4820439 (Hoechst AG). Especially preferred are compounds in which x = 2 and y = 0. The synthetic material is commercially available from Hoechst AG as S-Na<sub>2</sub> Si<sub>2</sub>O<sub>5</sub> (SKS6) and is described in US Patent No. 4664830.

The total amount of detergency builder in the granular composition ranges from 10 to 80 wt%, more preferably 10 to 45 wt%.

Detergent compositions according to the invention may also suitably contain a bleach system. This preferably comprises one or more peroxy bleach compounds, for example, inorganic persalts or organic peroxyacids, which may be employed in conjunction with bleach precursors to improve bleaching action at low temperatures.

The bleach system preferably comprises a peroxy bleach compound, preferably an inorganic persalt, optionally in conjunction with a precursor. Suitable persalts include sodium perborate monohydrate tetrahydrate and sodium percarbonate, with sodium percarbonate being most preferred.

Preferred bleach precursors are peracetic acid precursors, such as tetraacetylene diamine (TAED); and peroxybenzoic acid precursors, such as sodium benzoyloxybenzene sulphonate (BOBS).

Other materials which may be present in the detergent compositions of the invention include, for example, fluorescers, antiredeposition agents, inorganic salts such as sodium sulphate, other enzymes, lather control agents, fabric softening agents, pigments, coloured speckles and perfumes.

The detergent compositions of the invention may be prepared by any suitable method. The particulate detergent compositions are suitably prepared by any tower (spray-drying) or non-tower process.

In processes based around a spray-drying tower, a base powder is first prepared by spray-drying a slurry and then other components unsuitable for processing via the slurry can be

sprayed on or admixed (post-dosed). The enzyme will generally be post-dosed.

The zeolite MAP is suitable for inclusion in the slurry, although it may be advantageous for processing reasons for part of the zeolite MAP to be incorporated post-tower. The lamellar silicate, where this is employed, is also post-dosed.

Alternatively, particulate detergent compositions in accordance with the invention may be prepared by wholly non-tower processes such as granulation.

The granular detergent compositions of the invention may be prepared to any suitable bulk density. The compositions preferably have a bulk density of at least 400 g/l preferably at least 550 g/l, most preferably at least 700 g/l and, with particular preference at least 800 g/l.

The benefits of the present invention are particularly evident in powders of high bulk density, for example, of 700 g/l or above. Such powders may be prepared either by post-tower densification of spray-dried powder, or by wholly non-tower methods such as dry mixing and granulation; in both cases a high-speed mixer/granulator may advantageously be used. Processes using high-speed mixer/granulators are disclosed, for example, in EP340 013A, EP 367 339A, EP 390 251A and EP 420 317A (Unilever).

According to a further aspect of the invention there is provided a liquid detergent composition, preferably a heavy duty liquid detergent composition comprising a surfactant as previously described, a detergency builder comprising zeolite MAP and a cellulytic enzyme.

According to this embodiment the liquid detergent composition may be of any convenient physical form which may be aqueous or anhydrous. The term "liquid" used herein includes pasty viscous formulations such as gels. The liquid detergent system comprises, as the detergency builder zeolite MAP optionally in combination with other detergency builders such as fatty acids, citric acid or zeolite A.

A preferred co-builder is a lamellar sodium silicate such as SKS-6 which is particularly useful in pasty viscous formulations such as gels or in non-aqueous liquid detergents such as those described in WO92/16608 (Henkel).

The liquid detergent composition generally has a pH of from 6.5 to 10.5.

The total amount of detergency builder in the liquid composition is preferably from 5 to 70% of the total liquid composition.

The invention is illustrated by the following Example in which the abbreviations have the meanings defined below.

AS	:	Sodium alkyl sulphate
E05	:	C <sub>14</sub> -C <sub>15</sub> primary aliphatic ethoxylate alcohol having an average of 5 ethoxy groups per mole of alcohol.
Soap	:	tallow soap.
TAED	:	Tetraacetyl ethylene diamine.
DETPMP	:	Diethylene triamine penta (methylene phosphonic acid), marketed by Monsanto under the Trade Name Dequest 2060.
MA/AA	:	Copolymer of 1:4 maleic/acrylic acid (M <sub>w</sub> 80,000).
Citrate	:	Trisodium citrate dihydrate.
Antifoam granules	:	Mixture of silanated silica: silicone in ratio of 1:1.5 (M Wt 100,000).

#### Examples

Particulate components and compositions were prepared as follows:

	<u>1</u>	<u>2</u>	<u>3</u>
Anionic surfactant AS (C12-15)	9	-	-
AS (C12-14)	-	9	9
Nonionic surfactant E05	7	7	9
Soap	-	-	3
Zeolite MAP (anhydrous)	20	20	30
Sodium Carbonate	13	6	13
Sodium Bicarbonate	0	0	5
Amorphous sodium silicate	3	0	3
Crystalline sodium silicate	0	10	0
Citrate	2	0	5
Sodium Percarbonate	18	24	0
TAED granules	10	4	0
DETPMP	0.5	0.3	0.4
MA/AA	3	4	5
Antifoam granules	2	2	2
Enzyme Granules	2	2	2
Carezyme (1000 cevu/g)	0.15	0.20	0.10
Endolase (5000 cevu/g)		0.20	0.30
Moisture/Miscellaneous (Soil release agents, fabric whitening agents, perfumes, water)	balance	balance	balance
	100	100	100

The following Examples and Reference Examples demonstrate the reduced fabric encrustation after a repeated wash cycle of the detergent composition according to the invention

	<u>Ref 1</u>	<u>Ref 2</u>	<u>Ref 3</u>	<u>Example 4</u>	<u>Example 5</u>
Surfactant	14%	14%	14%	14%	14%
Zeolite A (d <sub>50</sub> = 3 microns)	35%	0%	0%	0%	0%
Micronised zeolite A (d <sub>50</sub> = 1 micron)	0%	35%	0%	35%	0%
Zeolite MAP (d <sub>50</sub> = micron)	0%	0%	35%	0%	35%
Carezyme at 1000 cevu/g	0%	0%	0%	1%	1%
Fabric ash (25 cycle washing)	1.0%	2.0%	2.0%	1.0%	1.0%

**CLAIMS:**

1. A detergent composition comprising:
  - (a) a surfactant selected from anionic, nonionic, cationic, amphoteric and zwitterionic detergent - active compounds and mixtures thereof;
  - (b) a detergency builder comprising zeolite P having a silicon to aluminium ratio not greater than 1.33 (zeolite MAP); and
  - (c) a cellulytic enzyme.
2. A detergent composition according to claim 1, wherein the zeolite MAP has a particle size ( $d_{50}$ ) of < 1.0 micrometre.
3. A detergent composition according to claim 2, wherein the zeolite MAP has a particle size ( $d_{50}$ ) of 0.4 to 1.0 micrometre.
4. A detergent composition according to any one of claims 1 to 3, wherein the zeolite MAP has a silicon to aluminium ratio not greater than 1.15.
5. A detergent composition according to claim 4, wherein the zeolite MAP has a silicon to aluminium ratio not greater than 1.07.
6. A detergent composition according to any one of claims 1 to 5, which comprises from 5 to 80% by weight of zeolite MAP.
7. A detergent composition according to any one of claims 1 to 6, which comprises the cellulytic enzyme in an amount to provide from 10 to 4000 cevu per 100 g of composition.

8. A granular detergent composition according to any of claim 1 to 7, which comprises from 5 to 60 wt % of component (a); from 10 to 80 wt% of component (b) and a cellulytic enzyme (c) in an amount to provide from 50 to 2000 cevu per 100 g of composition.
9. A liquid detergent composition according to any of claims 1 to 7 which comprises from 5 to 60 wt% of component (a); from 5 to 40 wt% of component (b); and a cellulytic enzyme (c) in an amount to provide from 100 to 200 cevu per 100 g of composition.
10. A detergent composition according to any one of claims 1 to 9, which comprises the cellulytic enzyme in an amount to provide from 10 to 4000 cevu per 100 g of composition.

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**Patents Act 1977**  
**Examiner's report to the Comptroller under Section 17**  
**(The Search report)**

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Application number  
**GB 9421220.6**

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**Relevant Technical Fields**

(i) UK CI (Ed.N)      C5D DHC DHZ DJA DJX

(ii) Int CI (Ed.6)      C11D

Search Examiner  
**M ELLIOTT**

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**Databases (see below)**

(i) UK Patent Office collections of GB, EP, WO and US patent specifications.

Date of completion of Search  
**20 JANUARY 1995**

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(ii)

Documents considered relevant following a search in respect of Claims :-  
**1-10**

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**Categories of documents**

**X:** Document indicating lack of novelty or of inventive step.

**P:** Document published on or after the declared priority date but before the filing date of the present application.

**Y:** Document indicating lack of inventive step if combined with one or more other documents of the same category.

**E:** Patent document published on or after, but with priority date earlier than, the filing date of the present application.

**A:** Document indicating technological background and/or state of the art.

**&:** Member of the same patent family; corresponding document.

Category	Identity of document and relevant passages		Relevant to claim(s)
X	EP 0552054 A1	(UNILEVER PLC) whole document	1 at least
X	EP 0521535 A1	(UNILEVER PLC) whole document	1 at least

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